②

AFOEHL REPORT 90-126SA00687HAE

AD-A227 489

DTIC FILE COPY

A Comparison of Three Prospective Analytical Methods for Benzene Analysis in Jet Fuel Environments

MOHAMMAD A. HOSSAIN, Major, USAF, BSC

August 1990

DTIC
ELECTE
OCT 0 9 1990
S E D

Final Report

Distribution is unlimited; approved for public release

90 10 05 016

NOTICES

When Government drawings, specifications, or other data are used for any purpose other than a definitely related Government procurement operation, the Government incurs no responsibility or any obligation whatsoever. The fact that the Government may have formulated, or in any way supplied the drawing, specifications, or other data, is not to be regarded by implication, or otherwise, as in any manner licensing the holder or any other person or corporation; or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

The mention of trade names or commercial products in this publication is for illustration purposes and does not constitute endorsement or recommendation for use by the United States Air Force.

The Public Affairs Office has reviewed this report, and it is releasable to the National Technical Information Service, where it will be available to the general public, including foreign nations.

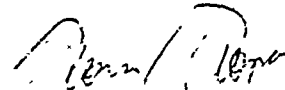This report has been reviewed and is approved for publication.

Air Force installations may direct requests for copies of this report to: Air Force Occupational and Environmental Health Laboratory (AFOEHL) Library, Brooks AFB TX 78235-5501.

Other Government agencies and their contractors registered with the DTIC should direct requests for copies of this report to: Defense Technical Information Center (DTIC), Cameron Station, Alexandria VA 22304-6145.

Non-Government agencies may purchase copies of this report from: National Technical Information Service (NTIS), 5285 Port Royal Road, Springfield VA 22161

MOHAMMAD A. HOSSAIN, Major, USAF, BSC
Chief, Occupational Chemistry Branch

THOMAS C. THOMAS, GM-15
Chief, Analytical Services Division

REPORT DOCUMENTATION PAGE

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden. to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204. Arlington, VA 22202 4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE July 1990	3. REPORT TYPE AND DATES COVERED Final

4. TITLE AND SUBTITLE
A Comparison of Three Prospective Analytical Methods for Benzene Analysis in Jet Fuel Environments

5. FUNDING NUMBERS

6. AUTHOR(S)
Mohammad A. Hossain, Major, USAF, BSC

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
AF Occupational and Environmental Health Laboratory
Brooks AFB TX 78235-5501

8. PERFORMING ORGANIZATION REPORT NUMBER
AFOEHL Report
90-126SA00687HAE

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Same as Blk 7

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Statement A. Unlimited, approved for public release

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Accurate analysis of benzene in jet fuel has been a concern over the past several years. The method we have been using to analyze benzene in jet fuel is the NIOSH 1501 method, a method specifically designed for aromatic hydrocarbons including benzene. However, the method is not designed for analysis of benzene in jet fuel environments. At the present time there is no approved (either by NIOSH or OSHA) method for analysis of benzene in fuel environments. At the request of HQ AAC/SGPB, we recently conducted a study to compare three prospective analytical methods (NIOSH method 1501 [GC/FID with packed column], modified NIOSH 1501 method [GC/FID with capillary column], and High Pressure Liquid Chromatography with Ultraviolet Detection [HPLC/UV]). In this study spiked charcoal tube samples as well as air samples of known concentrations of benzene in JP-4 and Stoddard Solvents were analyzed by all three methods. The test results showed that modified NIOSH 1501 and HPLC methods had good correlation between spiked and measured amount of benzene in JP-4 and Stoddard Solvent mixtures. The NIOSH 1501 method utilizing packed column over estimated the test benzene concentration indicating positive interference from other hydrocarbons present in JP-4 and Stoddard Solvents.

14. SUBJECT TERMS
Benzene   Gas Chromatograph   Packed Column   Jet Fuel
Capillary Column   High Pressure Liquid Chromatograph
Stoddard Solvent   Flame Ionization Detector , (JS)

15. NUMBER OF PAGES
20

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	none

ACKNOWLEDGEMENTS

Accession For		
NTIS GRA&I	X	
DTIC TAB	☐	
Unannounced	☐	
Justification		
By		
Distribution/		
Availability Codes		
Dist	Avail and/or Special	
A-1		

iii

Contents

I. INTRODUCTION

A. Background: HQ AAC/SGPB letter dated 20 Oct 89 requested the Air Force Occupational and Environmental Health Laboratory (AFOEHL) review and update the current analytical method for benzene in jet fuel environments to ensure the analytical results provided are representative. The letter also indicated that the National Institute for Occupational Safety and Health (NIOSH) method 1501 used for analysis of benzene in jet fuels identified unusually high workplace concentrations of benzene. The NIOSH 1501 method, specifically designed for aromatic hydrocarbons including benzene, utilizes a glass, 3.0 m x 2 mm, 10% OV-275 on 100/120 mesh Chromosorb W-AW or equivalent column in conjunction with the gas chromatography/flame ionization detector (GC/FID). This method is not designed for analysis of benzene in jet fuel environments. At the present time there is no approved (either by NIOSH or OSHA) method for analysis of benzene in fuel environments. However, the Occupational Safety and Health Administration (OSHA) laboratory at Salt Lake City, Utah utilizes a capillary column instead of a packed column as specified in the NIOSH method to analyze benzene in complex mixtures.

B. Our Consultative Letter, CL 89-131SA0687LAE dated 1 Dec 89 discussed the validity of the NIOSH method 1501 and other methods for analysis of benzene in complex mixtures such as jet fuel. The letter also stated that a study to compare three prospective methods (NIOSH method 1501 [Gas chromatography/flame ionization detector with packed column], OSHA method [GC/FID with capillary column], and high-pressure liquid chromatography with ultraviolet detection) would be accomplished.

II. STUDY PROCEDURES

A. Between December 1989 and June 1990 we conducted a study to compare three prospective analytical methods: NIOSH method 1501 (GC/FID with packed column), OSHA method (GC/FID with capillary column), and High Pressure Liquid Chromatography with Ultraviolet Detection (HPLC/UV). In this study, spiked charcoal tube samples with known amounts of benzene in JP-4 and in Stoddard solvents were analyzed by all three methods. Air samples with known concentrations of benzene in JP-4 vapor, generated in a dynamic flow dilution system at the industrial hygiene laboratory, were also collected in charcoal tubes and analyzed by the same methods. However, our air sampling study was somewhat limited.

B. For each test, two or more samples were prepared for each analytical method at the same concentrations.

III. ANALYTICAL METHODS

A. For HPLC analysis, Hewlett-Packard model 1084B liquid chromatograph equipped with a 254 nm UV detector was used. A Supelco 25 cm x 4.6 mm column of 5 um LC-PAH was used for separations. The mobile phase used was a mixture of water and acetonitrile. All spiked charcoal tubes were desorbed for 30 minutes in a 2 mL portion of 40% ethyl acetate in methylene chloride.

B. A Hewlett-Packard model 5880A gas chromatograph equipped with flame ionization detector was used for all GC analysis. Two separate columns (packed and capillary) were used to compare the separation of benzene in a complex mixture such as JP-4 & Stoddard solvents. The packed column was a Supelco 6.1 m (20 ft) x 3.2 mm (1/8 inch) stainless steel column of 10% FFAP on acid washed, 100/120 mesh Chromosorb W. The capillary column was a Supelco 30 m x 0.53 mm ID, DB-1 Wide Bore column with a 5 μm film thickness.

C. An Acculab model 8 Infrared Spectrometer (Beckman Instruments) with a 0.1 mm thickness Potassium Bromide (KBr) cell was used to determine benzene concentrations in JP-4 and Stoddard solvents. The percentage of benzene in bulk JP-4 and Stoddard solvents were measured as 0.53% and none detected, respectively.

IV. RESULTS AND DISCUSSION

· The test data and the analytical results are presented in Appendix A, Table I. The average, standard deviation, and coefficient of variation were calculated for each test and summarized in Appendix A, Table II. Linear regression lines and the 95% confidence limits for the predicted means were calculated for the relationship between the spiked amount and the measured amount of benzene for each analytical method and plotted in Figures 1, 2 & 3. The slopes, intercepts and correlation coefficients of regression lines between the spiked amount and measured amount of benzene for three analytical methods were: (a) slopes (0.73 for HPLC, 1.68 for GC/FID [packed column], and 1.10 for GC/FID [capillary column]); (b) intercepts (-5.80 for HPLC, 266 for GC/FID [packed column], and -4.47 for GC/FID [capillary column]); and (c) correlation coefficients (0.96 for HPLC, 0.43 for GC/FID [packed column], and 0.88 for GC/FID [capillary column]). These results indicated that HPLC and GC/FID (capillary column) methods had good correlation between the spiked and measured amount of benzene. The overall performances for GC/FID (packed column) was unsatisfactory. As is clear from Figure 2, the GC/FID (packed column) analytical data are scattered and well above the spiked amount over the range. This method overestimated the test benzene concentration indicating positive interference from other hydrocarbons present in the jet fuel environments. In fact, the packed column method reported large amounts (averaged 688.3 micrograms) of benzene for the spiked samples of Stoddard solvents (with no benzene) and failed to differentiate between benzene and other compounds of similar retention time as benzene.

Figure 4 presents regression lines for all three methods. The points shown in this figure are the spiked and measured amounts of benzene averaged for each set of tests.

Analysis of variance (ANOVA) and student's t distribution (t-test) were performed to test the hypothesis concerning the linearity, slope and intercept of regression line. All tests were performed at 95% confidence interval (i.e. inference of x = 0.05). Summaries of ANOVA, t-test and regression analysis for all three methods are shown in Appendix A, Table III. The GC/FID (packed column) data while accepting the null hypotheses of linearity and slope equals to one (b = 1) rejected hypothesis of intercept equals to zero (a = 0). The

intercept of 266 and correlation coefficient of 0.43 clearly indicated poor correlation and is unacceptable for analytical method of benzene in jet fuel environments. The HPLC and GC/FID (capillary column) data accepted the null hypothesis of linearity and correlated well (r = 0.96 & 0.88, respectively) with the spiked data. The HPLC data also accepted the hypothesis of intercept equals to zero (a = 0), but rejected the hypothesis of slope equals to one (b = 1). On the other hand, the GC/FID (capillary column) data accepted both hypotheses of intercept equals to zero (a = 0) and slope equals to one (b = 1). We accept both HPLC and GC/FID (capillary column) methods as valid for the analysis of benzene in jet fuel environments. However, it is clearly evident that the GC/FID (capillary column) method provided better accuracy than the HPLC method.

V. CONCLUSIONS

On the basis of the test results, the following was concluded:

1. The NIOSH method 1501 utilizing GC/FID with packed column showed positive interference in analyzing benzene in jet fuel environments and thereby could lead to incorrect exposure assessments for workers.

2. Both HPLC and modified NIOSH method 1501 utilizing capillary column provided reasonable accuracy in determining benzene concentration in a JP-4 environment.

3. The GC/FID (capillary column) method showed a better accuracy than the HPLC method while comparing the test and the measured concentrations of benzene in jet fuel environments.

4. The lower detection limits of benzene using HPLC and GC/FID (capillary column) methods were noted as four and two micrograms, respectively. Based on these detection limits, the minimum sample volumes required to detect one-tenth of PEL for benzene (3.0 mg/m^3) were calculated as 13.3 and 6.7 liters (L), respectively.

5. Since the HPLC utilizing a UV detector set at 254 nm will not detect aliphatic or alicyclic hydrocarbons, the measurement of total hydrocarbons in jet fuel environments need to be performed by another method such as GC/FID (capillary column) method.

6. The GC/FID (capillary column) method will be able to measure both benzene and total hydrocarbons in jet fuel environments.

VI. RECOMMENDATIONS

A. Based on the results of this study, we recommend the use of the modified NIOSH 1501 method (GC/FID with capillary column) for analyzing benzene in jet fuel environments or other complex mixtures. The minimum recommended sample volume specified in the NIOSH method 1501 should be

increased to 6.7 liters instead of 2 liters for a detection limit of one-tenth of benzene PEL (i.e., detection limit of 0.3 mg/m³). If lower sensitivity is accepted, the following sample volumes will be required:

Minimum Sample Volume	Detection Limit
3.3 liters	20% PEL (i.e. 0.60 mg/m³)
2.7 liters	25% PEL (i.e. 0.75 mg/m³)
1.4 lites	50% PEL (i.e. 1.50 mg/m³)

    B. Modify the 1989 Sampling Guide (pages III-10, 11) with the following information:

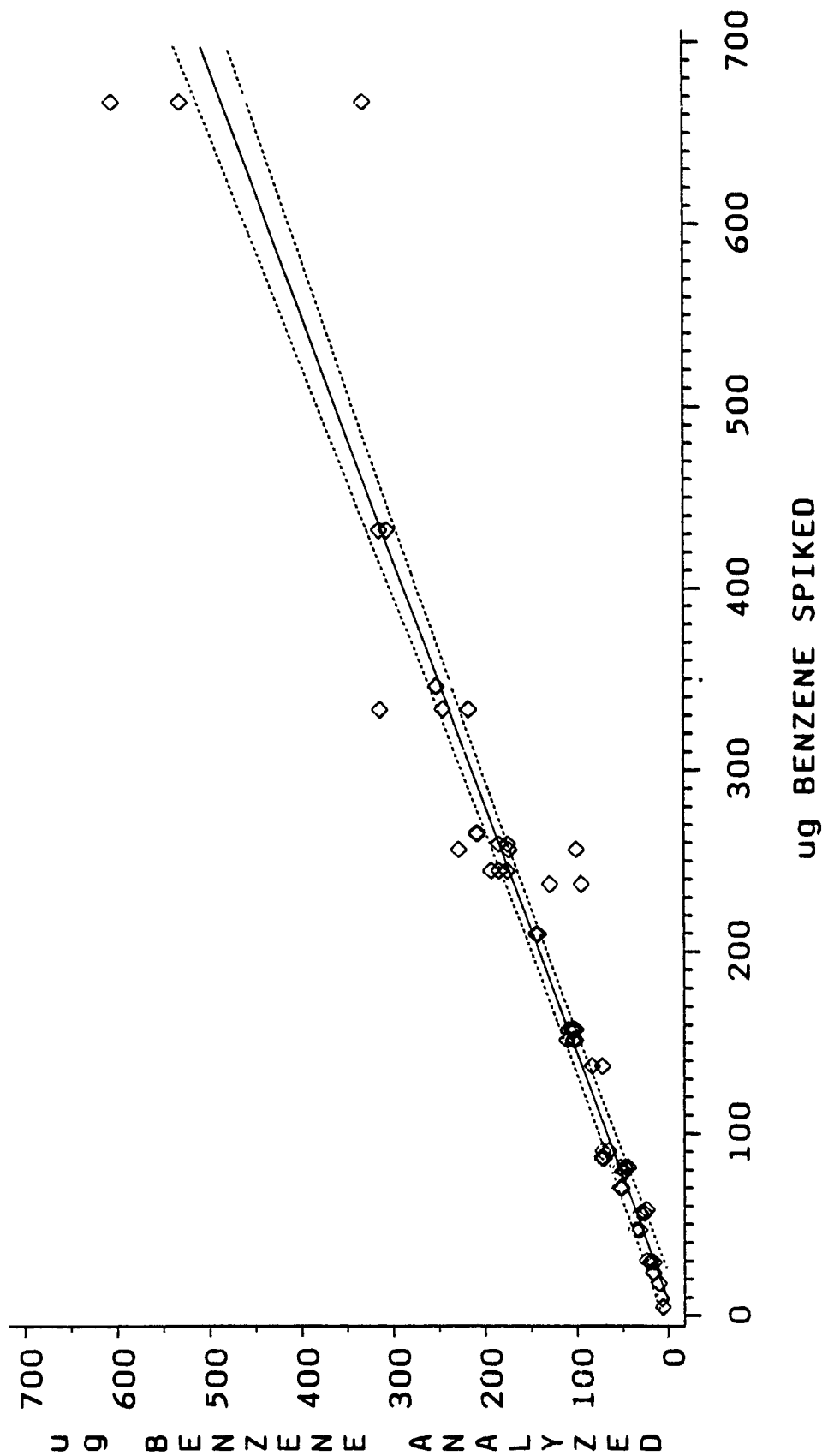| NAME	COLLECTION METHOD	SAMP RATE MIN - MAX		RECMD VOL MIN - MAX		NOTES	REMARKS	REFERENCE
Benzene	CTXX-101	0.02	0.2	6.7	- 30	J	6.7L sample volume is required for a detection limit of 0.3 mg/m³. For lower sensitivity, such as 0.75 mg/m³ detection limit (25% PEL), 2.7L sample volume is required.	Modified N1501C

SPIKED VS MEASURED BENZENE BY HPLC

Figure 1. Spiked vs measured benzene by HPLC. The solid line is the linear regression line and the broken lines are the 95% confidence limits for the predicted means.

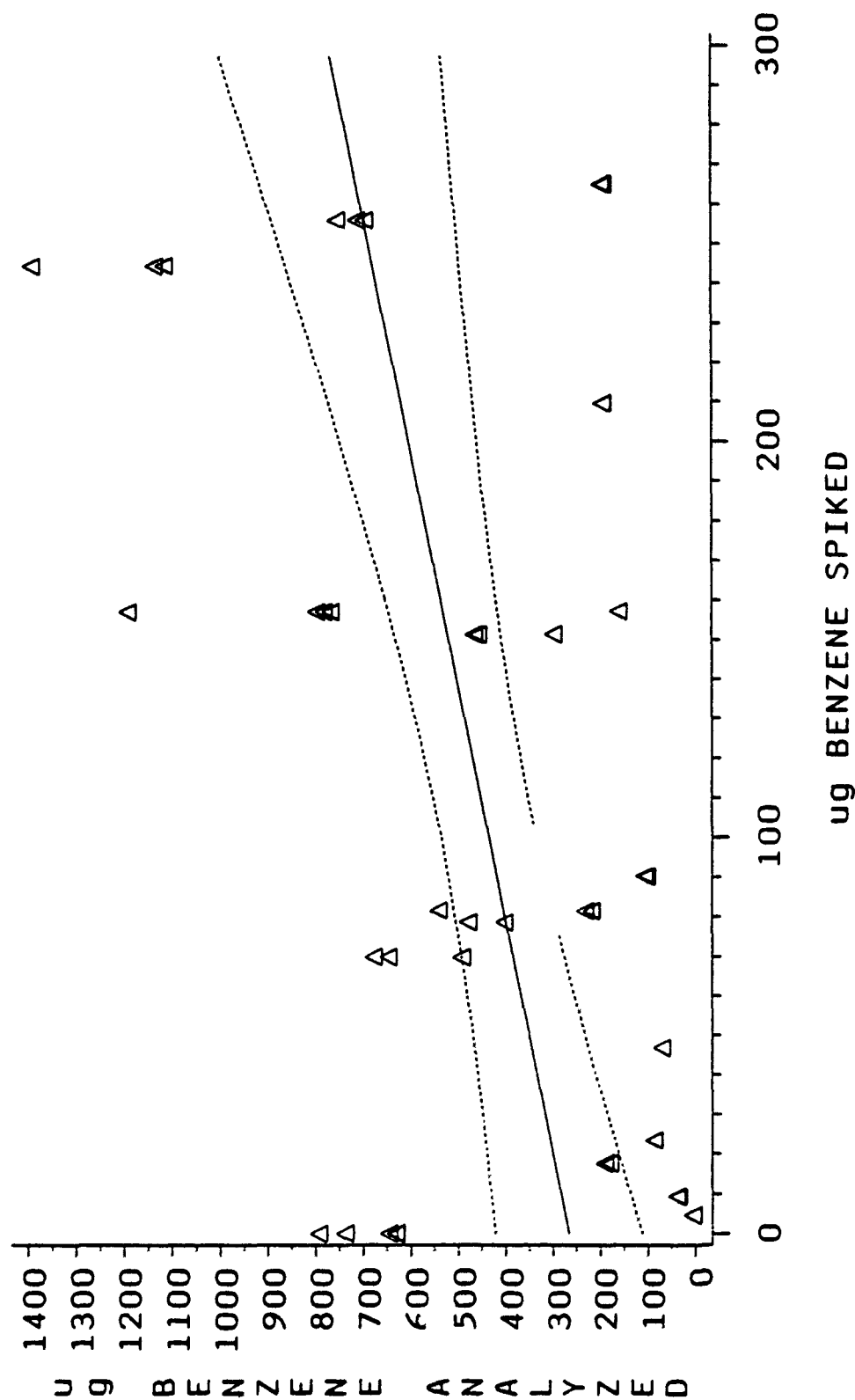# SPIKED VS MEASURED BENZENE BY GC/FID [PACKED COLUMN]

Figure 2. Spiked vs measured benzene by GC/FID [packed column]. The solid line is the linear regression line and the broken lines are the 95% confidence limits for the predicted means.
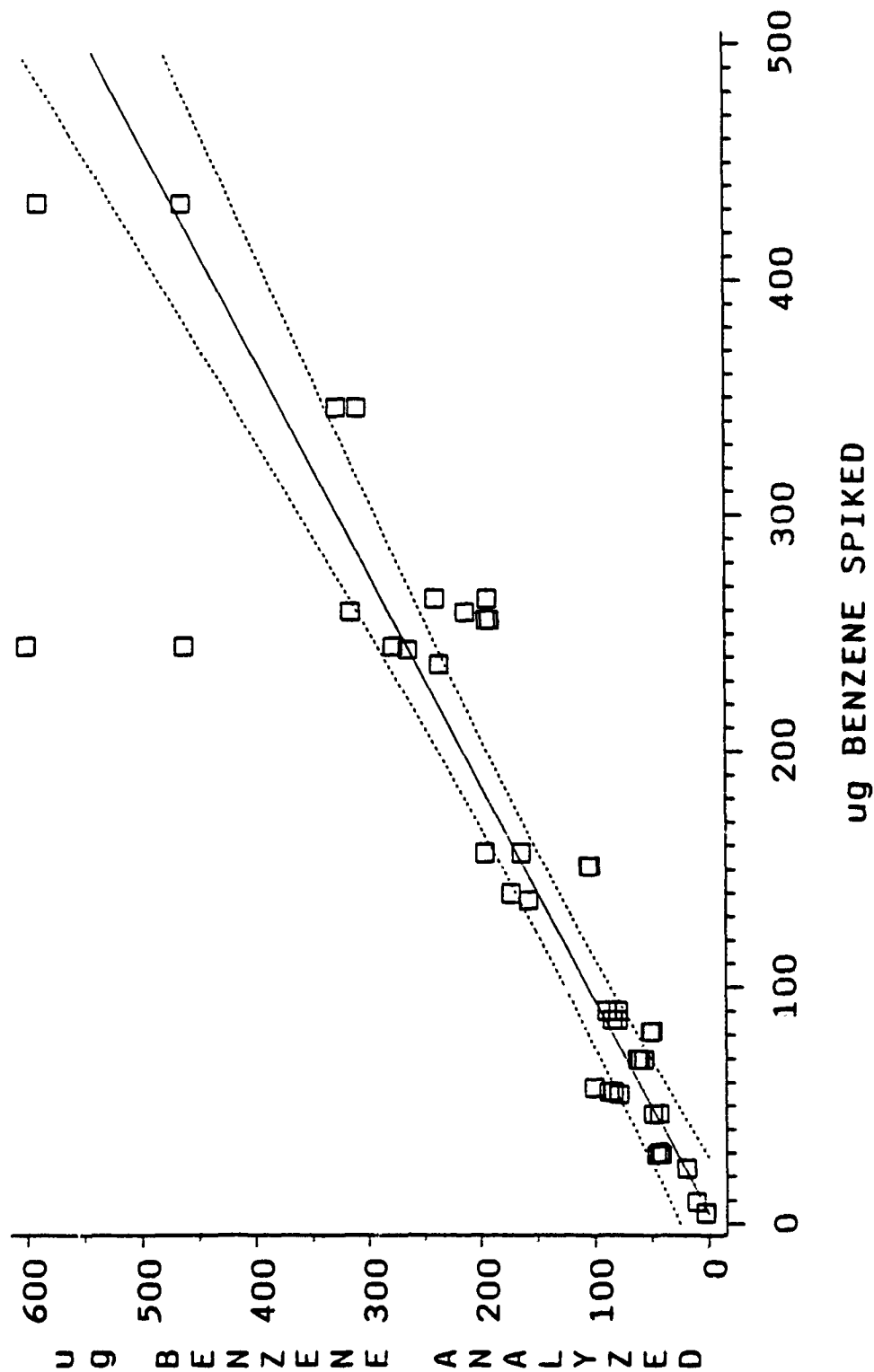
Figure 3. Spiked vs measured benzene by GC/FID [capillary column]. The solid line is the linear regression line and the broken lines are the 95% confidence limits for the predicted means.
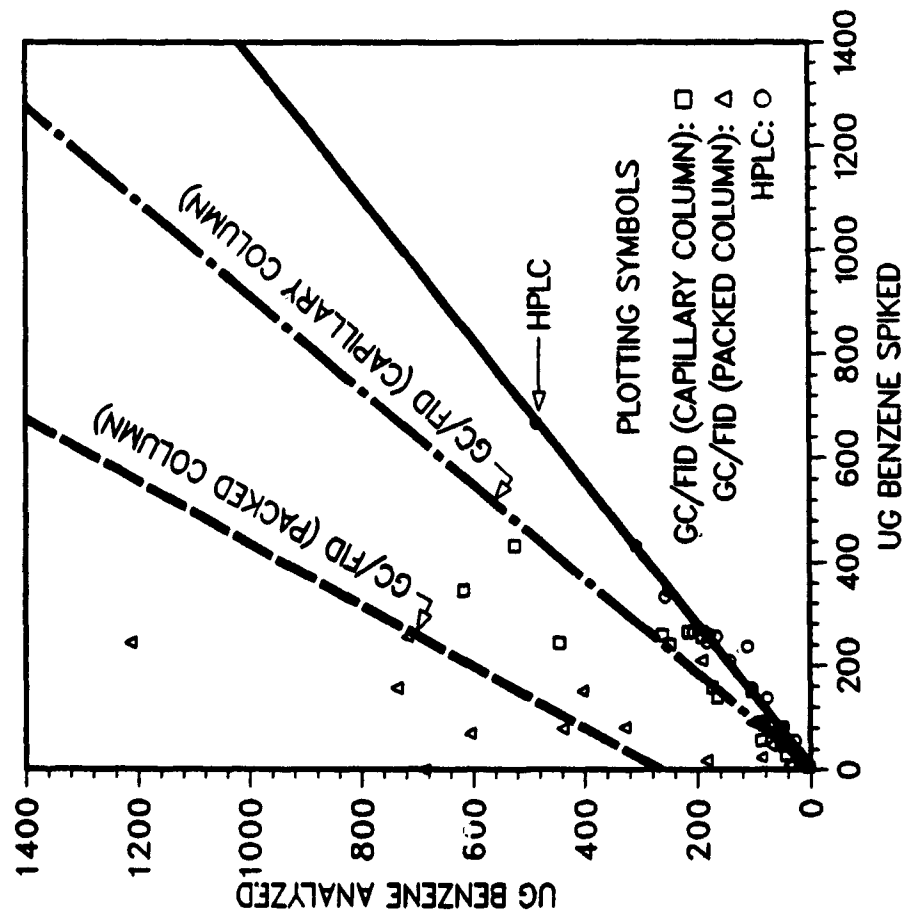
SPIKED VS MEASURED BENZENE

Figure 4

Appendix A

Test Results and Statistical Analysis

(This page left blank)

Table I

Test Results
for
JP-4/Benzene Study

Methods	Actual Amount of Benzene, µg	Measured Amount of Benzene, µg		
		Analytical Methods		
		HPLC	GC/FID (packed column)	GC/FID (capillary column)
JP-4 (@ 0.53% Benzene) Spiked in Charcoal Tube	4.7	5.8	5.5	3.0
	4.7	5.2	5.7	2.5
	4.7	<4*	5.2	2.8
	9.3	6.9	39.4	11.0
	9.3	6.7	35.9	11.0
	23.3	17.0	88.7	19.4
	23.3	15.6	86.2	19.5
	46.6	31.6	70.9	49.0
	46.6	35.6	70.0	43.3
JP-4 + Known Amount of Benzene Spiked in Charcoal Tube	81.5	47.1	231.1	51.2
	81.5	52.4	540.6	50.1
	81.5	43.7	217.2	49.2
	90.2	65.3	101.9	88.9
	90.2	71.7	106.4	79.2
	151.4	103.0	296.0	104.2
	151.4	101.2	464.0	105.1
	151.4	110.0	455.3	103.2
	256.1	99.5	710.1	194.2
	256.1	172.9	752.0	191.5
	256.1	227.0	693.4	190.8
	264.9	206.6	194.6	239.0
	264.9	208.2	190.0	192.6

Table I Cont'd

Methods	Actual Amount of Benzene, µg	Measured Amount of Benzene, µg		
		Analytical Methods		
		HPLC	GC/FID (packed column)	GC/FID (capillary column)
Stoddard Solvent (No Benzene) Spiked in Charcoal Tube	0	<4*	632.6	<2*
	0	<4*	630.7	<2*
	0	<4*	646.0	<2*
	0	<4*	738.4	-
	0	<4*	793.8	-
Stoddard Solvent (with Known Amount of Benzene) Spiked in Charcoal Tube	17.5	10.1	179.7	-
	17.5	9.5	190.1	-
	69.8	50.6	646.9	60.4
	69.8	51.5	492.6	62.6
	69.8	53.3	677.5	56.9
	78.6	48.4	477.7	-
	78.6	50.2	401.7	-
	86.4	70.4	-	79.7
	86.4	73.4	-	84.2
	157.1	101.0	794.7	-
	157.1	102.1	159.4	-
	157.1	104.8	765.3	163.5
	157.1	108.3	1191.0	163.7
	157.1	103.9	780.0	195.3
	209.5	141.4	193.7	-
	209.5	143.7	192.4	-
	244.4	192.1	1113.0	599.3
	244.4	183.3	1134.0	461.3
	244.4	174.6	1391.0	276.4
	259.2	183.8	-	313.8
	259.2	174.3	-	212.4
	345.6	251.5	-	325.7
	345.6	250.9	-	307.7
	432.1	303.8	-	461.7
	432.1	312.3	-	587.8

Table I Cont'd

Methods	Actual Amount of Benzene, µg	Measured Amount of Benzene, µg		
		Analytical Methods		
		HPLC	GC/FID (packed column)	GC/FID (capillary column)
Blank	0	<4*	11.1*	-
	0	<4*	10.6*	-
	0	<4*	<2*	<2*
Known Amount of	333	215.7	-	-
Benzene were	333	244.2	-	-
collected in Charcoal	333	311.9	-	-
Tubes using Vapor				
Generation System	667	600.7	-	-
	667	328.4	-	-
	667	527.0	-	-
	30	23.6	-	43.8
	29	20.1	-	43.7
	29	19.2	-	41.4
	29	15.7	-	42.1
	29	-	-	46.2
	58	23.6	-	100.4
	56	25.8	-	87.3
	56	30.6	-	83.5
	55	-	-	78.6
	137	82.9	-	157.2
	137	71.6	-	-
	140	-	-	172.8
	237	94.3	-	235.7
	237	128.3	-	-
	243	-	-	263.3

* sample results not included in the statistical analysis.

13

Table II

Statistical Analysis
JP-4/Benzene Study

Methods	Actual Amount of Benzene (µg)	Measured Amount of Benzene, µg		
		Analytical Methods		
		HPLC Avg. ± S.D. CV (%)	GC/FID (packed column) Avg. ± S.D. CV (%)	GC/FID (capillary column) Avg. ± S.D. CV (%)
JP-4 (@ 0.53% Benzene) Spiked in Charcoal Tube	4.7	5.5 ± 0.4 7.7	5.5 ± 0.3 4.6	2.8 ± 0.3 9.1
	9.3	6.8 ± 0.1 2.1	37.7 ± 2.5 6.6	11.0 ± 0 0
	23.3	16.3 ± 1.0 6.1	87.5 ± 1.8 2.0	19.5 ± 0.1 0.4
	46.6	33.6 ± 2.8 8.4	70.5 ± 0.6 0.9	46.2 ± 4.0 8.7
JP-4 + Known Amount of Benzene Spiked in Charcoal Tube	81.5	47.7 ± 4.4 9.2	329.6 ± 183 55.5	50.2 ± 1.0 2.0
	90.2	68.5 ± 4.5 6.6	104.2 ± 3.2 3.1	84.1 ± 6.9 8.2
	151.4	104.7 ± 4.6 4.4	405.1 ± 94.6 23.3	104.2 ± 1.0 0.9
	256.1	166.5 ± 64.0 38.4	718.5 ± 30.2 4.2	192.2 ± 1.8 0.9
	264.9	207.4 ± 1.1 0.5	192.3 ± 3.3 1.7	215.8 ± 32.8 15.2
Stoddard Solvent (No Benzene) Spiked in Charcoal Tube	0	<4	688.3 ± 73.9 10.7	<2

Table II Cont'd

Methods	Actual Amount of Benzene (µg)	HPLC Avg. ± S.D.	CV (%)	GC/FID (packed column) Avg. ± S.D.	CV (%)	GC/FID (capillary column) Avg. ± S.D.	CV (%)
Stoddard Solvent (with Known Amount of Benzene) Spiked in Charcoal Tube	17.5	9.8 ± 0.4	4.3	184.9 ± 7.4	4.0	-	
	69.8	51.8 ± 1.4	2.7	605.7 ± 99.1	16.4	60.0 ± 2.9	4.8
	78.6	49.3 ± 1.3	2.6	439.7 ± 53.7	12.2	-	
	86.4	71.9 ± 2.1	3.0	-		82.0 ± 3.2	3.9
	157.1	104.0 ± 2.8	2.7	738.1 ± 369	50.0	174.2 ± 18.3	10.5
	209.5	142.6 ± 1.6	1.1	193.1 ± 0.9	0.5	-	
	244.4	183.3 ± 8.8	4.8	1213 ± 155	12.8	445.7 ± 162	36.4
	259.2	179.1 ± 6.7	3.8	-		263.1 ± 71.7	27.3
	345.6	251.2 ± 0.4	0.2	-		616.7 ± 12.7	4.0
	432.1	308.1 ± 6.0	2.0	-		524.8 ± 89.2	17.0
Known Amount of Benzene were collected in charcoal Tubes Using Vapor Generation System	333	257.3 ± 49.4	19.2	-		-	
	667	485.4 ± 141	29.0	-		-	
	29.3	19.7 ± 3.2	16.5	-		-	
	29.2	-		-		43.4 ± 1.9	4.3
	56.7	26.7 ± 3.6	13.4	-		-	
	56.3	-		-		87.5 ± 9.3	10.7
	137.0	77.3 ± 8.0	10.3	-		-	
	138.5	-		-		165.0 ± 11.0	6.7
	237.0	111.3 ± 24.0	21.6	-		-	
	240	-		-		249.5 ± 19.5	7.8

Note: Avg. = Average of two or more spiked samples
S.D. = Standard Deviation
CV = Coefficient of Variation

15

Table III

Least-Square Fit and Regression Analysis of Test Data

Least-Squares	HPLC vs Spiked (n=63)	GC/FID* (p.c) vs Spiked (n=44)	GC/FID** (c.c) vs Spiked (n=52)
Slope, b	0.73	1.68	1.10
Intercept, a	-5.80	266	-4.47
Correlation Coefficient, r	0.963	0.428	0.881
Inference (x=0.05)			
Linear	Accept	Accept	Accept
b=1 (Slope)	Reject	Accept	Accept
b=0 (Slope)	Reject	Reject	Reject
a=0 (Intercept)	Accept	Reject	Accept

 * p.c = packed column
** c.c = capillary column

Distribution List

	Copies
HQ USAF/SGPA Bolling AFB DC 20332-6188	1
HQ AFSC/SGPB Andrews AFB DC 20334-5000	1
HQ AFLC/SGPB Wright-Patterson AFB OH 45433-5001	1
HQ AFSPACECOM/SGB Peterson AFB CO 80914-5001	1
HQ ATC/SGPB Randolph AFB TX 78150-5001	1
HQ MAC/SGPB Scott AFB IL 62225-5001	1
HQ PACAF/SGPB Hickam AFB HI 96853-5001	1
HQ SAC/SGPB Offutt AFB NE 68113-5001	1
HQ TAC/SGPB Langley AFB VA 23665-5578	1
HQ USAFE/SGPB APO New York 09094-5001	1
HQ USAF Academy/SGPB Colorado Springs CO 80840-5470	1
HQ AFRES/SGPB Robins AFB GA 31098-6001	1
ANGSC/SGPB Andrews AFB DC 20331-6008	1
USAF Regional Hospital Elmendorf/SGPB Elmendorf AFB AK 99506-5300	1
HQ HSD/XA Brooks AFB TX 78235-5000	1
7100 CSW Medical Center/SGB APO New York 09220-5300	1

Distribution List Cont'd

Copies

Det 1, AFOEHL
APO San Francisco 96274-5000   1

USAFSAM/TSK/ED/EDH/EDZ
Brooks AFB TX 78235-5301   1 ea

Defense Technical Information Center (DTIC)
Cameron Station
Alexandria VA 22304-6145   2